1,158,163

PATENT SPECIFICATION

NO DRAWINGS

1,158,163

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Date of filing Complete Specification: 9 June, 1967.

Application Date: 15 June, 1966. No. 26693/66

Complete Specification Published: 16 July, 1969.

Index at Acceptance:—C3 P (2C16B, 2C20B, 2C20C, 2D1A, 2D8, 2K7, 2K8, 7C16B, 7C20B, 7C20C, 7D2A1, 7D8, 7K2, 7K8, 8C16B, 8C20B, 8C20C, 8D3A, 8D8, 8K2, 8K7, 10C16B, 10C20B, 10C20C, 10D1A); C3 B (1C6X, 1C10, 1C12, 1C23, 1D2C, 1L4C); C3 R (3N7, 22C5B1, 22N3, 2C6X, 2C10, 2C12, 2C14A, 2C22, 2C23, 2C27, 2C28X, 2L1B, 2L2CX, 2L4C, 3C6X, 3C10, 3C12, 3C14A, 3C22, 3C23, 3C27, 3C28X, 3L1B, 3L2CX, 3L4C, 22C6X, 22C10, 22C12, 22C14A, 22C22, 22C23, 22C27, 22C28X, 22L1B, 22L2CX, 22L4C, 27K2C6X, 27K2C10, 27K2C12, 27K2C14A, 27K2C22, 27K2C23, 27K2C27, 27K2C28X, 27K2L1B, 27K2L2CX, 27K2L4C, 29C6X, 29C10, 29C12, 29C14A, 29C22, 29C23, 29C27, 29C28X, 29CL1B, 29CL2CX, 29CL4C).

Int. Cl.:—C 08 f 45/00.

COMPLETE SPECIFICATION

Improvements in or relating to Polymer Compositions

We, BERK LIMITED, a British Company, of Berk House, 8 Baker Street, London, W.1., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with improvements in or relating to polymer compositions and, more particularly, with certain specific thermoplastic and thermosetting polymer compositions having fire retardant properties.

We have discovered that the fire retardant properties of certain polymers are improved by incorporating therein a small proportion of certain halogenated aryl compounds and, according to the present invention, we provide polymer compositions having fire retardant properties which comprise at least one polyamide, polyimide, polycarbonate, polyether, polyformaldehyde, polyvinyl acetal, epoxide resin, melamine/formaldehyde resin, urea/formaldehyde resin, silicone, cellulose ester, polyvinyl-chloride resin, acrylonitrile butadiene styrene synthetic rubber co-polymer, acrylonitrile styrene synthetic rubber co-polymer and/or a natural rubber and, as a fire retardant, at least one compound of the formula:

Ar $(Br)_m(Cl)_nR$ and/or $Ar(Br)_y(Cl)_xOR$

where Ar is an aromatic hydrocarbon residue, m is 3 or more, n is 0, 1 or 2, x is 0 or an integer, y is 3 or more with the proviso that when x is 0 and R is hydrogen, y is 3, and R is hydrogen or a hydrocarbon group which may be a straight or branched chain alkyl or alkenyl group, any of which may be halogenated, an aryl group which may be halogenated in the nucleus or an aralkyl group which may be halogenated in the nucleus or side chain.

The term polyamide as used herein includes glass reinforced polyamides. Particular cellulose esters include cellulose acetates in the form of fibres or shaped products and especially preferred polyvinyl chloride resins are plasticised polyvinyl chlorides.

The proportion of fire retardant to be used will depend upon the nature of the polymer (some, for instance, such as polyvinyl chloride, have inherent fire retardancy), the total halogen content of the fire retardant used and the degree of fire retardancy desired of the polymer composition, i.e. whether it is desired to obtain a self-extinguishing or non-burning composition.

Generally it is necessary to add the fire retardant compound in an amount sufficient to give a total bromine content of at least 3% by weight of the polymer, although a total bromine content of less than 3% by weight can be used with certain polymers having inherent fire retardancy, such as polyvinyl chloride. It is norm-

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ally preferred to have a higher bromine content within the range of 5 to 10% by weight of the polymer; it is generally uneconomic to have a bromine content of more than 20% by weight of the polymer.

Examples of fire retardant compounds for use in accordance with the invention include tetrabromobenzene, pentabromotoluene, tribromophenol, pentabromophenyl, allyl ether, pentabromophenyl-n-propyl ether, the various isomers of tribromotoluene and tribromophenyl allyl ether and hexabromodiphenyl ether.

The effectiveness of the fire retardant compound can be enhanced by also incorporating antimony oxide in the polymer composition. It has been found that at least 1 part by weight of antimony oxide per 8 parts by weight of fire retardant is necessary to increase measurably the fire retardancy of the polymer composition as compared with the same polymer composition in which the fire retardant has been incorporated alone. It is preferred to add antimony oxide in the range of from 0.5 to 1.5 : 1 by weight of the fire retardant compound. Greater increase in fire retardancy can be achieved with a weight ratio of antimony oxide to fire retardant of 2 or more : 1.

The fire retardant compound (and antimony oxide, if used) can be incorporated at any suitable stage in the manufacture of the polymer composition. Thus the fire retardant compound may be added to a monomer prior to polymerisation or, as may often be more convenient, to an already formed polymer. Other conventional constituents of the above-mentioned polymer compositions, such as fillers, plasticisers, pigments and stabilisers may also be incorporated.

In order that the invention may be more fully understood the following examples are given by way of illustration only. All parts are by weight unless otherwise stated.

Example 1

60 parts of "Rilsan" ZMO, (trade mark; a glass fibre filled nylon 11 sold by Fisons Industrial Chemicals Ltd.), 3.3 parts of antimony oxide and 3.3 parts of pentabromotoluene were mixed together in the manner described below in a small, oil heated internal mixer (a Brabender Plastograph).

The Brabender Plastograph essentially comprises a mixing chamber surrounded by an oil-filled jacket; rotors are provided in the mixing chamber. The oil bath was set at a temperature of 230°C and the rotor speed was set at 20 r.p.m. After the rotors had been running for ten minutes the "Rilsan" ZMO was added to the mixing chamber. Immediately after fluxing, the pentabromotoluene and antimony oxide were added and the rotor speed was increased to 50 r.p.m. Mixing was continued for 4 minutes and thereafter the rotor speed was reduced to 10 r.p.m. The mixture was removed from the mixing chamber and transferred to a 6" × 4" × $\frac{1}{8}$" picture frame mould which was positioned between two 12" × 12" × $\frac{1}{16}$" steel plates, each of which was faced with a polyester film. The mould sandwich thus formed was crushed in a steam heated press, whilst cold, to compact the polymer composition prior to moulding. The mould sandwich was then preheated for 2 minutes at 220°C in an electrically heated press under light pressure. The pressure was gradually increased over a period of about 30 seconds to 1250 pounds per square inch and this pressure was maintained for a further 90 seconds. The mould sandwich was then transferred to a water cooled steam heated press and pressed under a pressure of 450 pounds per square inch for two minutes. The mould sandwich was removed from the press and the panels formed were left to condition at 23°C overnight.

The flammability of the moulded panels was tested using ASTM test procedure D 635 — 56T with two exceptions, namely:—

1. Only three or five specimens were tested
2. A "on-burning/self extinguishing" class was introduced to cover the case where a specimen catches alight but does not burn as far as the first line.

Using this modified test the results were as shown in Table 1 below. The flammability classifications given are those provided in the ASTM test with the exception (2) above. The test was discontinued after the first three specimens tested were found to be "burning".

Comparative Test 1

60 parts of "Rilsan" ZMO were moulded in a mould sandwich in the same manner as that used in Example 1, without the addition of fire retardant or antimony oxide.

The flammability of the moulded material was tested using the modified ASTM test used in Example 1. The rate of burning was 0.79 inches per min. and the material was classified as "burning". The test was discontinued after three specimens had been tested since all three were classified "burning".

Example 2

60 parts of "Rilsan" ZMO, 7.5 parts pentabromotoluene and 7.5 parts antimony oxide were mixed together, moulded and tested in the same manner as described in Example 1. Five specimens were tested. The results obtained are given in Table 1 below.

Example 3

60 parts of "Rilsan" ZMO, 12.9 parts pentabromotoluene and 12.9 parts of antimony oxide were mixed, moulded and tested in the same way as described in Example 1. The fire retardancy results obtaned are given in Table 1 below:—

Table 1

Example	*Number of specimens*	*% Sb_2O_3*	*% pentabromotoluene*	*% Bromine*	*Rate of burning inches/minute*	*Extent of burning in inches*	*Flammability classification*
1	3	5.5	5.5	4.4	0.53	—	Burning
2	5	12.5	12.5	10.0	—	2.2	Self-extinguishing
3	5	21.5	21.5	17.4	—	0.8	Non-burning/self-extinguishing

WHAT WE CLAIM IS:—

1. A polymer composition having fire retardant properties, which comprises at least one polyamide, polyimide, polycarbonate, polyether, polyformaldehyde, polyvinyl acetal, epoxide resin, melamine/formaldehyde resin, urea/formaldehyde resin, silicone, cellulose ester, polyvinylchloride resin, acrylonitrile butadiene styrene synthetic rubber co-polymer, acrylonitrile styrene synthetic rubber co-polymer and/or a natural rubber and, as a fire retardant, at least one compound of the formula:

$Ar(Br)_m(Cl)_nR$ and/or $Ar(Br)_y(Cl)_zOR$

where Ar is an aromatic hydrocarbon residue, *m* is 3 or more, *n* is 0, 1 or 2, x is 0 or an integer, *y* is 3 or more with the proviso that when *x* is 0 and R is hydrogen, *y* is 3, and R is a hydrogen or a hydrocarbon group which may be a straight or branched chain alkyl or alkenyl group, any of which may be halogenated, an aryl group which may be halogenated in the nucleus or an aralkyl group which may be halogenated in the nucleus or side chain.

2. A composition according to claim 1, in which the amount of fire retardant incorporated is such as to provide a total bromine content of at least 3% by weight of the polymer component.

3. A composition according to claim 2, in which the total bromine content is from 5 to 10% by weight of the polymer component.

4. A composition according to any of claims 1 to 3, in which the fire retardant is tetrabromobenzene, pentabromotoluene, tribromophenol, pentabromophenyl allyl ether, pentabromophenyl-n-propyl ether, tribromotoluene, tribromophenyl allyl ether and/or hexabromodiphenyl ether.

5. A composition according to any of claims 1 to 4, which additionally contains at least 1 part by weight of antimony oxide per 8 parts by weight of fire retardant.

6. A composition according to claim 5, in which the weight ratio of antimony oxide to fire retardant is from 0.5 to 1.5 : 1.

7. A polymer composition according to claim 1 substantially as herein described in any of the Examples.

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Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1969.
Published at the Patent Office, 25 Southampton Buildings, London, W.C.2. from which copies may be obtained.